ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Thermodynamic Parameters For Adsorption of Some Disperse Dyes From Industrial Wastewater on Carbon Soot

H. F. El-Gamal[1], F. K. M. Wali[2]* and K. H. Khalil[3]

1. Public Work Engineering Department, Faculty of Engineering, Mansoura University, Mansoura, Egypt.
2. Department of Chemistry, The Prince Sultan Industrial College, Al Kharj, Saudi Arabia.
3. Civil Engineering Department, Higher Institute of Engineering, Shorouk Academy, Egypt.

Manuscript Info

Manuscript History:

Received: 16 October 2014
Final Accepted: 26 November 2014
Published Online: December 2014

Key words:
Adsorption; Thermodynamic parameters; Freundlich model; Dubinin-Radushkevick equation and wastewater treatment.

***Corresponding Author**

F. K. M. Wali
farook19702001@yahoo.com

Abstract

Wastewaters of three disperse dyes obtained from a dyeing unit were subjected to color removal by adsorption technique onto carbon soot (a bi-product during partial oxidation of natural gas) as a cheap alternative for conventional carbon adsorbents. Freundlich isotherm was used to describe the adsorption of dyes from the industrial wastewater. Dubinin-Radushkevick equation was also used to evaluate the adsorption process. The processes were carried out at different temperatures between 25^{o}C to 60^{o}C and Van't Hoff equation was used to evaluate thermodynamic parameters (ΔH, ΔS) for the interpretation of the adsorption process.
.

Introduction

Application of adsorption in municipal wastewater treatment falls into two categories: tertiary treatment and physical-chemical treatment (PCT). Tertiary treatment is the term used when adsorption is applied to removal of residual organic materials remaining in the effluent of biological treatment processes. Physical-chemical treatment processes are those in which raw wastewater is exposed to physical or chemical treatment prior to carbon adsorption. In such cases, adsorption alone rather than biological treatment is responsible for removal of dissolved organic impurities. Adsorption is used in industrial wastewater treatment to remove color and organic materials such as dyes, phenols, detergents, cresols, or other toxic or non-biodegradable materials [1-5].

Adsorption is the concentration of a substance at the surface [4,5]. The adsorption at a surface or interface is largely a result of binding forces between atoms, molecules, and ions of the adsorbate on the surface [6]. The commercial adsorbents used today for the removal of metals from solutions include a variety of clays, activated carbon, gels, alumina, silica, zeolites, and other resinous materials [7–11].

The first major interest is the selection of adsorbent that show higher capacity and adsorption rate and low price. The second interest is to clearly identify the mechanism of the adsorption process and how to accelerate the process to be effective.

Carbon soot which is a solid bi-product resulting from partial oxidation of natural gas in Talkha Fertilizers and Chemical Plants (SEMADCO Egypt now named as Delta for Fertilizers Production) is a promising material for different industrial applications as a substitute for commercial powdered activated carbon [12-14].

1. Materials and Methods

All chemicals and solvents used in this study were of the highest grade of purity (spectral grade). Three commercial disperse dyes (listed in Table 1) were chosen for studying their adsorption behavior on carbon soot at different temperatures. Industrial wastewater samples of these dyes were obtained from Al-Amel dyeing unit for dying fabrics and textiles, which is located at Sandoub city near El-Mansoura, Egypt. Carbon soot, which is produced as a result of partial oxidation of natural gas, was obtained from El-Delta for fertilizers Co. (SEMADCO).

Experimental procedures, according to Standard Methods [22], were carried out to study the adsorption of this dyed stuff from wastewater by using a shaker with water bath controlling temperature. The remaining concentration was measured using a spectrophotometer (Qualen Kamp Visible-Spec SPR-590-010-W). The separation of adsorbents from solutions was performed by centrifugation using a bench top centrifuge model T-54.

2. Results and Discussion

The adsorption trend of the three disperse dyes onto carbon soot was fitted to the Freundlich isotherm. The Freundlich model is also a non-linear model that suggests a mono layer sorption of the metal on the biomass. The Freundlich model assumes a heterogeneous energetic distribution of the active binding sites on the sorbate surface with interactions between the adsorbed molecules [4, 8 and 15]. In the Freundlich model, it is considered that the binding sites affinities on the biomass surface vary with the interactions between the adsorbed molecules. Consequently, the sites with stronger affinity are occupied first [4,8]. The general equation and the linearized form for the Freundlich isotherm are expressed as follows:

$$q_e = K_F C_e^{1/n} \quad (1)$$

$$\text{Ln } q_e = \ln K_F + 1/n \ln C_e \quad (2)$$

In equations (1) and (2), K_F is the maximum adsorption capacity (mol. g^{-1}), q_e quantity of dye adsorbed at equilibrium over mass of adsorbent, C_e amount of dye adsorbed at equilibrium and n is the adsorption intensity, which is related to the affinity or binding strength [4,8]. K_F and 1/n are determined from the slope and intercept resulting from plotting ln (q_e) versus ln (C_e) as shown in figures (1 to 3), the adsorption capacity and affinity of carbon soot for dyes was determined with the Freundlich model.

Table 1: Color and maximum wavelength for the tested dyestuffs

Dye	Color	Wavelength (nm)
Disperse dye MTD	Blue	613
Disperse red 167	Red	460
Disperse orange 25	Orange	427

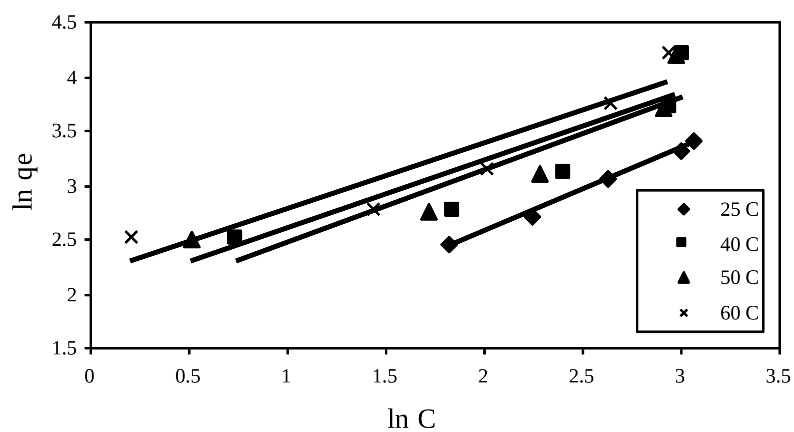

Figure 1: Freundlich isotherms for the adsorption of disperse dye MTD on carbon soot at different temperatures.

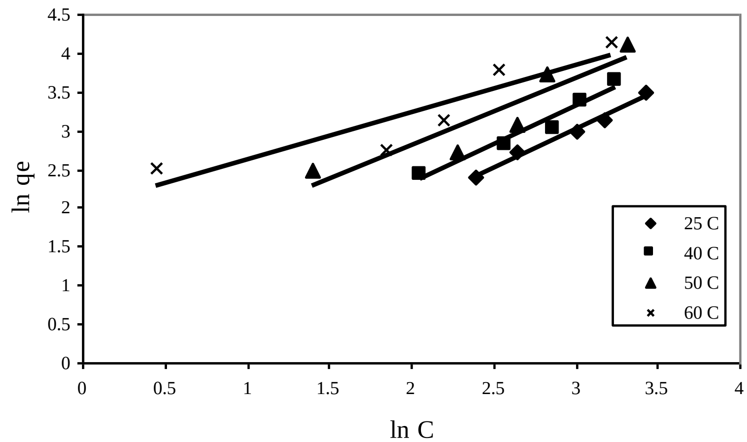

Figure 2: Freundlich isotherms for the adsorption of disperse red 167 on carbon soot at different temperatures.

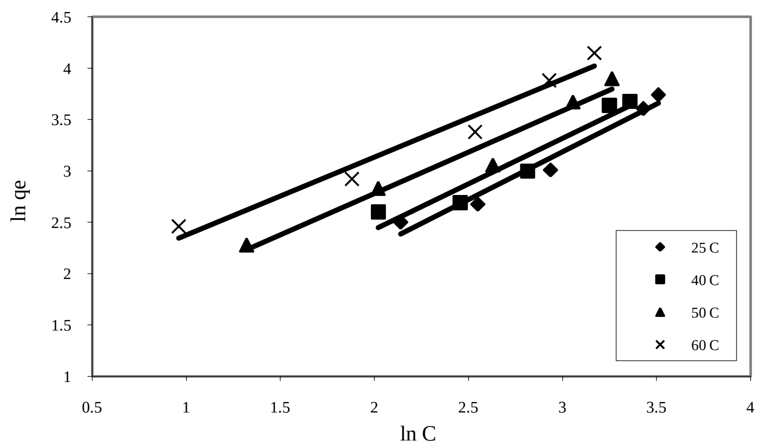

Figure 3: Freundlich isotherms for the adsorption of Disperse orange 25 on carbon soot at different temperatures.

From the slope and intercept, the values of n (intensity of adsorption) and K_F (maximum adsorption capacity) were calculated respectively and delineated and documented as shown in table 2.

Table 2: Freundlich parameters for the adsorption of dyes on carbon soot at different temperatures

Dye	Température (^{o}C)	Soot n	Soot K_F	Soot R
Disperse dye MTD	25	1.32	2.89	0.90
	40	1.50	5.99	0.99
	50	1.61	7.15	9.94
	60	1.66	8.74	0.97
Disperse red 167	25	1.04	1.03	0.96
	40	1.02	1.41	0.963
	50	1.28	2.85	0.985

	60	1.66	7.56	0.992
Disperse orange 25	25	1.06	1.49	0.965
	40	1.13	1.93	0.958
	50	1.24	3.21	0.905
	60	1.32	5.04	0.966

The K_F values obtained from the Freundlich model suggests that the dye molecules binding affinity was in the order disperse dye MTD > disperse red 167 > disperse orange 25. It is found that n values are in the range that indicates a good adsorption since n values are higher than unity [17, 19 and 21]. Moreover these data revealed that there is a direct relation between adsorption capacity and temperature. The delineated data shows that adsorption capacity value (K_F) increases as the temperature increases from (25 to 60^{o}C).

The adsorption equilibrium data fitted well at all temperatures with the Freundlich model. This suggests that the adsorption process follows a monolayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules.

The correlation coefficients (R^2) obtained from the Freundlich model were ranging from 0.901 and 0.992 for the adsorption process, this suggests that the adsorption system of carbon soot could have more than one functional group which is responsible for the binding of dye molecule to active sites of adsorption on carbon soot [4,19].

Determination of thermodynamic parameters

Dubinin-Radushkevick equation has been used for the determination of micro pore volume and thereby surface area of micro porous carbons. This equation assumes a constant sorption potential [4, 15 and 23]. The linear presentation of this equation is expressed by:-

$$\text{Ln } q_e = \text{Ln } q_m - K_E \epsilon^{o2} \quad (3)$$

$$\epsilon^o = RT \ln (1+1/ C_e) \quad (4)$$

Where, ϵ^o is the Polanyi potential, q_m is the monolayer capacity (mol. g^{-1}), q_e quantity of dye adsorbed at equilibrium over mass of adsorbent, and K_E is a constant related to adsorption energy (mol^2. K. J^{-2}). The q_m and K_E parameters can be obtained from the intercept and slope of the ln q_e against ϵ^{o2} curves shown in figures (4 to 6).

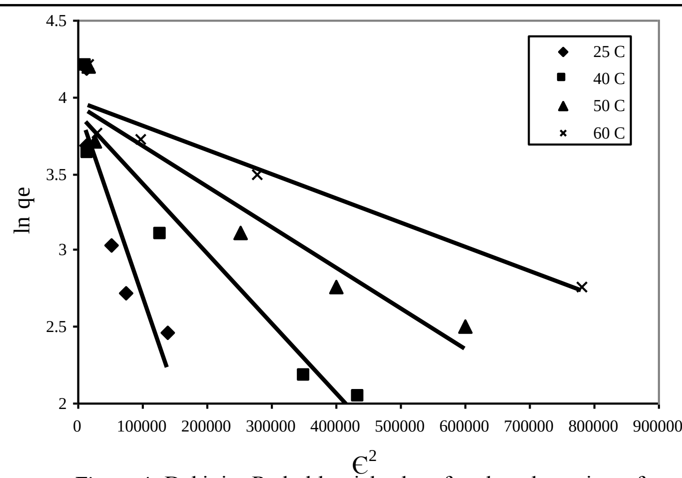

Figure 4: Dubinin–Radushkevick plots for the adsorption of disperse dye MTD on carbon soot at different temperatures.

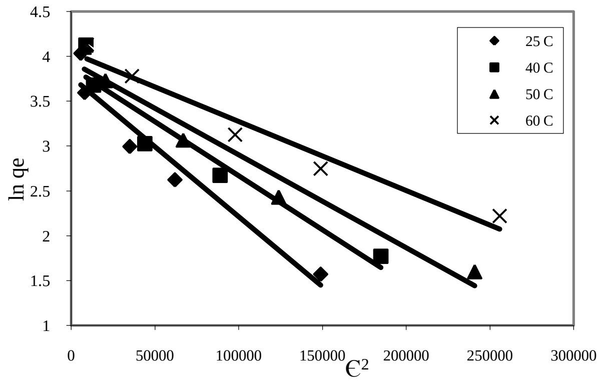

Figure 5: Dubinin–Radushkevick plots for the adsorption of disperse red 167 on carbon soot at different temperatures.

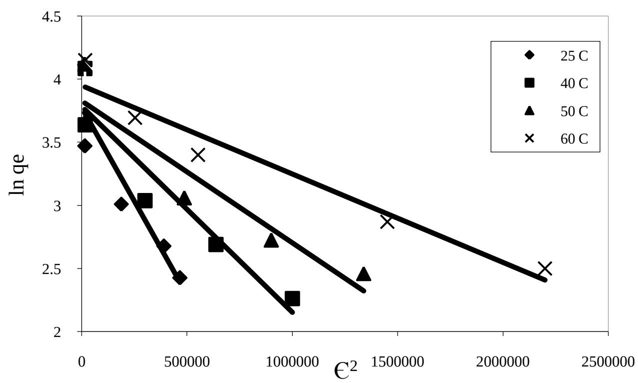

Figure 6: Dubinin–Radushkevick plots for the adsorption of Disperse orange 25 on carbon soot at different temperatures.

The mean free energy of adsorption (E) is the free energy change when one mole of ions is transferred to the surface of the membrane from infinity in the solution [4, 15 and 19] and it is calculated from:-

$$E = (-2K_E)^{-1/2} \quad (5)$$

The Dubinin–Radushkevick parameter (q_m) and mean free energies (E) which represent the mean free energy of sorption per molecule of sorbate [4], were calculated and listed in table 3. The magnitude of E is useful for estimating the type of sorption reaction, since E < 8 kJ. mol^{-1}, physical forces such as diffusional processes may affect the sorption mechanism [4, 15 and 19]. So, the adsorption of dyes on carbon soot seems to be a complex phenomenon, where diffusion and chemical bonding occur at different temperature ranges, this may support that the monolayer capacity (q_m) increases with increasing temperature for all dyes.

Table 3: Dubinin–Radushkevick parameters for the adsorption of dyes on carbon soot at different temperatures

Dye	Temperature °C	q_m mol/kg	E joule/mol	r
Disperse dye MTD	25	40.7	288.67	0.8117
	40	49.127	316.22	0.9286
	50	51.527	408.25	0.9045
	60	53.043	500.00	0.9023
Disperse red 167	25	45.107	158.11	0.9368
	40	50.987	223.61	0.9215
	50	53.901	223.61	0.9588
	60	55.648	250.00	0.9591
Disperse orange 25	25	46.895	408.25	0.8566
	40	52.451	500.00	0.9061
	50	55.319	707.11	0.8983
	60	57.869	785.16	0.9476

The thermodynamic functions such as enthalpy change (ΔH^o) and entropy change (ΔS^o), were determined using Van't Hoff equation [16, 20, 21 and 24]:-

$$\ln K_c = \Delta S^o/R - (\Delta H^o/R)\ 1/T \qquad (6)$$

Equation (6) represents a straight line with two variables, K_c and 1/T as shown in figure 7. By plotting ln K_c versus 1/T the values of ΔH^o can be calculated from the slope (slope = $\Delta H^o/R$) and ΔS^o can be calculated from the intercept of that line (intercept = $\Delta S^o/R$). The values of the equilibrium constant (K_c) at different temperatures were calculated from the following equation [10, 16, 20, 21 and 24]:-

$$K_c = K_1/K_2 = (C_{Bo} + C_{Ao}\ X_{Ae}) / (C_{Ao} + C_{Ao}\ X_{Ae}) \qquad (7)$$

Where, C_{Ao} : initial concentration of solute in solution at time, t = 0.

C_{Bo} : initial concentration of solute in the sorbent at time, t = 0.

X_{Ae} : fraction of solute adsorbed at equilibrium condition, and

Kc : equilibrium constant.

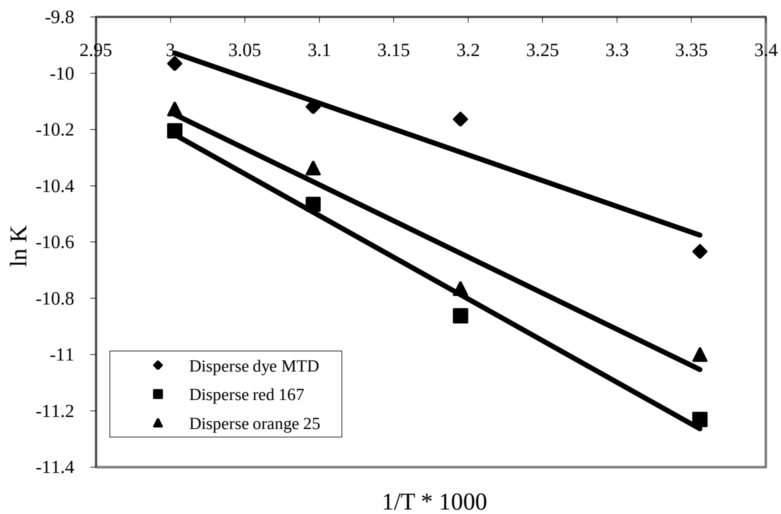

Figure 7. Vant'Hoff plot for the adsorption of dyes on carbon soot.

The free energy change (ΔG^o) parameter was calculated from equation 8 [10, 13, 17, 18 and 24]:-

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (8)$$

From these plots of Van't Hoff equation, the values of enthalpy changes (ΔH^o) and entropy change (ΔS^o) were determined from the slopes (equal $\boldsymbol{\Delta H^o/R}$) and intercepts (equal $\boldsymbol{\Delta S^o/R}$) and are listed in table 4.

Table 4: Thermodynamic parameters for the adsorption of dyes on carbon soot at different temperatures

Dye	ΔH Kcal/mol	ΔS Kcal/mol
Disperse dye MTD	3.636666	-8.73675
Disperse red 167	5.095332	-4.78883
Disperse orange 25	5.870304	-2.6037

Investigation of the obtained values of the enthalpy shows that the adsorption processes of the selected dyestuffs on carbon soot are endothermic this is in accordance with increasing adsorption rate with increasing temperature [10, 16, 20 and 21]. The negative value of entropy means the reduction of degree of freedom of the adsorbed dyes, this suggests that disorder decreases at the solid liquid interface during the adsorption of dyes [24].

3. Conclusions

Carbon soot used for color removal of dyes from industrial wastewater samples yielded very good efficiency ranging from (92-98) %, consequently, carbon soot can used for color removal of dyes from industrial wastewater discharged from dying units. The following conclusions can be evaluated from this study:-

- Freundlich model suggests that the dye molecules binding affinity was in the order disperse dye MTD > disperse red 167 > disperse orange 25. In addition, the adsorption equilibrium data fitted well at all temperatures with the Freundlich model. This suggests that the adsorption process follows a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules.
- The Dubinin–Radushkevick parameter (q_m) and mean free energies (E) revealed that, adsorption of dyes on carbon soot seems to be a complex phenomenon, where diffusion and chemical bonding occur at different temperature ranges, this may be supported by the monolayer capacity (q_m) increase with increasing temperature for all dyes.
- Thermodynamic parameters indicate that all adsorption processes are endothermic this is in agreement with the increasing adsorption capacity with increasing temperature.

- The negative value of entropy means the reduction of degree of freedom of the adsorbed dyes, this suggests that disorder decreases at the solid liquid interface during the adsorption of dyes.

4. References

[1] A. Ghoniem. and K. H. Khalil , "Utilization of COD and color removal for treating carpet industry wastewater", 5th Mansoura International Engineering Conference, (2006), Sharm El-Sheikh, March, Egypt.

[2] C. F. Gurnham, "Industrial waste control ", Academic Press, (1965), New York.

[3] X. Hu, L. Lei, G. Chen and P. L. Yue, "On the degradability of printing and dyeing wastewater by wet air oxidation", Water Research, 35(8) (2001) 2078-2080.

[4] Maather F. Sawalha, Jose R. Peralta-Videa, Jaime Romero-Gonza´lez, Maria Duarte-Gardea , Jorge L., and Gardea-Torresdey J.L, "Thermodynamic and isotherm studies of the biosorption of Cu(II), Pb(II), and Zn(II) by leaves of saltbush (Atriplex canescens) " J. Chem. Thermodynamics, 39 (2007) 488–492.

[5] A. Altindag, S. Yigit, Chemosphere 60(4) (2005) 552–556, as cited in reference 4.

[6] P. Kar, M. Misra, J. Chem. Technol. Biotechnol., 79(11) (2004) 1313–1319, as cited in reference 4.

[7] G. Tylko, Z. Banach, J. Borowska, M. Niklinska, E. Pyza, Microsc. Res. Tech., 66 (5) (2005) 239–247, as cited in reference 4.

[8] T. A. Davis, B. Volesky, A. Mucci, Water Res., 37(18) (2003) 4311–4330, as cited in reference 4.

[9] J. L. Gardea-Torresdey, G. de la Rosa, J. R. Peralta-Videa, Pure Appl. Chem., 76(4) (2004) 801–813, as cited in reference 4.

[10] F. K. M. Wali, "synthesis of some new pyrazolone dyestuffs and evaluation of their adsorption properties on carbon" M.Sc. Thesis Faculty of Science, (2000) , Damietta, Mansoura University, Egypt.

[12] J. C. Igwe, and A. A. Abia "A bioseparation process for removing heavy metals from waste water using biosorbents" , African Journal of Biotechnology, 5(12) (2006) 1167-1179.

[12] I. G. A. Rashed, H. R. Lotfy, M. A. El-Komy and M. A. Metwally, "Buffering effect of PAC on biodegradability of phenol", Proc. of 2nd Int. Conf. On Environmental Protection Is a Must, (1992), Alex. Univ., Egypt; 24-27 Feb. 417-429.

[13] A. M. Abdallah, M. E. Kalifa and I. G. A. Rashed, "Removal of environmental ammonia pollution from Talkha Fertilizer and chemical plants using carbon soot", Proc. of 2nd Chem. Conf., 27-29 Sept. (1998), Fac. Sci., Mansoura University; Egypt, 329-338.

[14] I. G. A. Rashed, M. A. El-Komy, A. A. Al-Sarway, R. Mostafa and S. Al Bashir "Physical chemical treatment of wastewater produced from partial oxidation of natural gas", Journal of Environmental Science, (1994) University of Mansoura, Egypt, 8, 12-18.

[15] J. Romero-Gonzalez, J. R. Peralta-Videa, E. Rodriguez, S. L. Ramirez, and J. L. Gardea-Torresdey, "Determination of thermodynamic parameters of Cr(VI) adsorption from aqueous solution onto Agave lechuguilla biomass", J. Chem. Thermodyn., 37(4) (2005) 343–347.

[16] I. G. A. Rashed, M. A. Hanna, A. A. Al-sarawy, and F. K. M. Wali, "Removal of some 4-pyrazolone dyes from aqueous solutions by adsorption onto different types of carbon", Journal of Desalination, 186 (2005) 129-153.

[17] A. A. Al-Sarway, "Removal of soluble organic materials from water by carbon adsorption and / or other materials", Ph.D. Thesis, (1994), Faculty of Science, Mansoura University; Egypt.

[18] L. D. Benfield, J. F. Judkins and B. L. Weand "process chemistry for water and wastewater Treatment", Prentice Hall Inc., (1982), Englewood Cliffs, New Jersey.

[19] R. S. Juang, S. H. Lin and K. H. Tsao, J. Colloid Interface Sci., 254 (2002) 234–241, as cited in reference 15.

[20] K. Banerjee, P. N. Cheremisinoff and S. L. Cheng "Adsorption kinetics of o-xylene by flyash", Water Research, 31(2) (1997) 249-261.

[21] M. I. Attia, "Removal of some heavy metals from water", Ph.D. Thesis, (1999), Faculty of Science (Damietta),

Mansoura University; Egypt.

[22] APHA, AWWA and WPCF, "Standard methods for the examination of water and wastewater ", 18th Edition, (1992), American Public Health Association, Washington, DC.

[23] Raj K Vyas, Shashi and Surendra Kumar, "Determination of micro pore volume and surface area of zeolite molecular sieves by D-R and D-A equations: a comparative study" Indian Jourrnal of Chemical Technology, September, 11 (2004) 704-709.

[24] Dragan Djordjevic, Dejan Stojkovic, Novica Djordjevic and Miodrag Smelcerovic "Thermodynamics of reactive dye adsorption from aqueous solution of the ashes from city heating station" Ecological Chemistry and Engineering; 18(4) (2011).